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SOME OBSERVATIONS ON THE ELECTRON-MICROSCOPIC FRACTOGRAPHY OF EMBRITTLED STEELS

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SOME OBSERVATIONS ON THE ELECTRON-MICROSCOPIC FRACTOGRAPHY OF EMBRITTLED STEELS

by

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INTRODUCTION

A number of conditions of heat treatment, stress, and environment have been shown to promote intergranular fracture in high-strength quenched and tempered steels. Among these conditions are:

(1) Hydrogen-stress cracking

(2) Stress-corrosion cracking

(3) Quench cracking

(4) Early stages of fatigue cracking

(5) 500 F embrittlement

(6) Temper brittleness.

These phenomena have been recognized for some time, but generally speaking, no satisfactory theories or explanations concerning the occurrence of the observed intergranular weaknesses have been presented. However, metallurgical research has indicated the conditions that lead to brittleness or cracking and by avoiding these conditions design engineers are enabled to employ the superior properties of these materials.

Electron-microscopic fractography has recently been employed to study intergranular fracture in high-strength steels and, as a result, much interesting and useful information has been obtained. In the present memorandum, information is presented from studies using electron-microscopic fractography in the examination of fractures in high-strength steels that have been treated to produce 500 F embrittlement and temper brittleness.

500 F Embrittlement

In carbon and alloy steels, 500 F embrittlement, also known as tempered-martensite embrittlement, manifests itself as an inordinately low impact resistance after tempering in the temperature range from about 400 to almost 800 F. Within the past few years, there has been an increasing demand for steels having the strength properties that are developed by tempering in this range. Before such steels could be

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used, ways of minimizing or avoiding 500 F embrittlement were needed. Research at that time indicated that the addition of about 1.5 per cent silicon to a steel such as AISI 4340 shifted the embrittling range upward in temperature. This shift made it possible to temper in the temperature range which normally caused 500 F embrittlement. The resultant high strength could be utilized with less danger of brittle fracture resulting from an impact load. It was also found that 500 F embrittlement could be avoided by using very short tempering treatments.[1, 2]

Any theory of the mechanism of 500 F embrittlement must explain a number of observed characteristics:

(1) 500 F embrittlement causes a low room-temperature impact energy and a relatively high transition temperature after tempering in the vicinity of 500 to 600 F.

(2) Embrittlement is revealed in the impact properties, but not in the hardness, normal tensile properties, nor seemingly in the fracture toughness, K_{Ic}.

(3) The addition of silicon or the use of short or very long tempering cycles can eliminate embrittlement[1, 2].

(4) Embrittlement is not present in steels made from high-purity melting stock.[3] Addition of trace amounts of P, As, Sb, Sn, or larger amounts of Mn to a high-purity steel has been shown to promote embrittlement.

(5) Martensitic steels are susceptible to 500 F embrittlement, but bainitic steels are not.

Electron-microscopic fractography has been applied to the study of 500 F embrittlement by Spretnak and Bucher.[4] Figure 1, from their work, is a curve showing the room-temperature impact energy as a function of tempering temperature for AISI 4340 steel. Note the characteristic dip in the curve in the 400 to 800 F temperature range. Also shown on the curve are the relative percentages of cleavage, dimpled rupture, and intergranular fracture obtained at each tempering temperature. These values were obtained by visual estimation during electron-microscopic examination of replicas of the crack-propagation regions of the Charpy bars. It is evident that the low-impact values in the embrittlement range are associated with the presence of significant proportions of grain-boundary or intergranular fracture. Another series of specimens was fractured at liquid-nitrogen temperature, and results very similar to those shown in Figure 1 were obtained. Figure 2 shows the typical appearance of fractures in steels tempered in the embrittlement range; no unusual precipitates or grain-boundary films can be seen on the grain facets.

Edwards and Beachem have studied the fracture surface appearance as a function of yield strength in a series of AISI 4300 steels using the electron microscope.[5] Figure 3 summarizes some of their results and shows the visually estimated percentage of grain-boundary fracture in round notched tensile bars as a function of yield strength for steels of three carbon contents. The peak in intergranular fracture occurs at yield strengths that would be developed by tempering in the embrittling range. Again, in this study, no grain-boundary precipitates were observed.

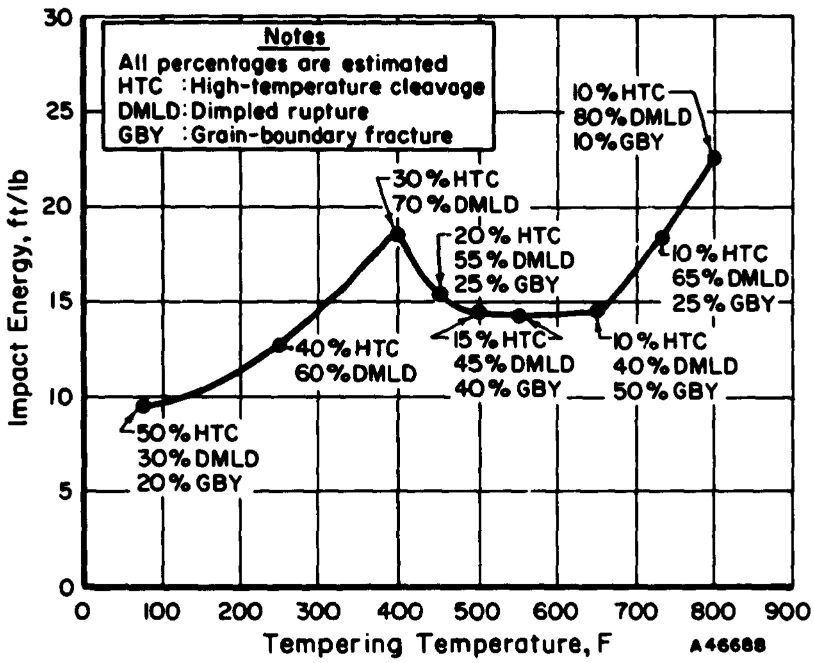


FIGURE 1. IMPACT ENERGY AS A FUNCTION OF TEMPERING TEMPERATURE FOR AISI 4340 STEEL, V-NOTCHED CHARPY BARS, AUSTENITIZED FOR 1 HOUR AT 1550 F, OIL QUENCHED AND TEMPERED 2 HOURS AT THE INDICATED TEMPERATURES, AND FRACTURED AT ROOM TEMPERATURE(4)

Approximate percentages of cleavage, dimpled, and grain-boundary fracture are given for each point.

FIGURE 2. ELECTRON-MICROSCOPIC FRACTOGRAPH OF 500 F EMBRITTLED AISI 4340 STEEL SHOWING PREDOMINANTLY INTERGRANULAR FRACTURE(4)

(Tempering temperature: 550 F, fractured at -320 F)

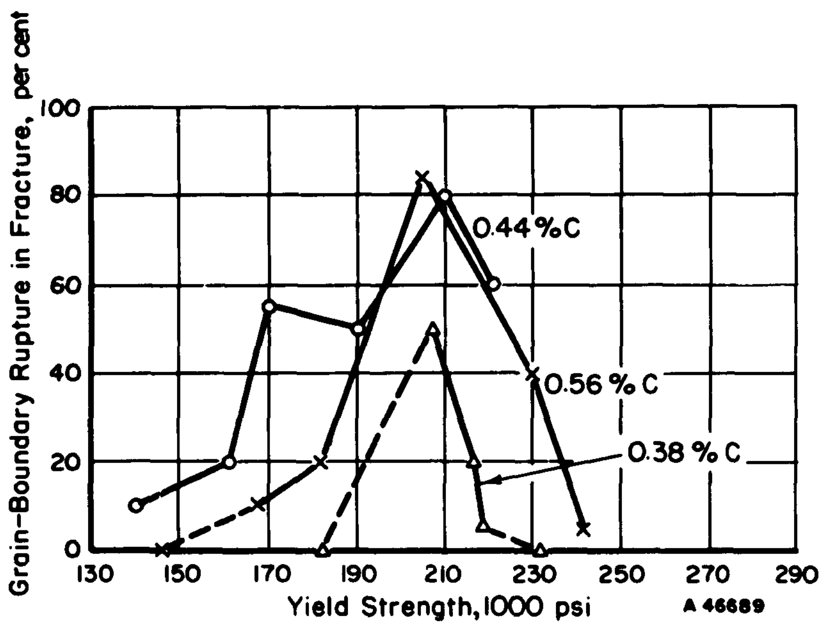


FIGURE 3. VARIATION IN PER CENT OF GRAIN-BOUNDARY RUPTURE WITH YIELD STRENGTH IN NOTCHED ROUND TENSILE SPECIMENS OF THREE CARBON CONTENTS[5]

It is interesting to note that 500 F embrittlement is not observed in fracture-toughness tests on specimens containing fatigue cracks, but is most readily observed in impact tests employing specimens with relatively blunt notches.[6] This observation may indicate that 500 F embrittlement is related to crack-initiation rather than to crack-propagation. The fact still remains, however, that 500 F embrittlement results in an intergranular fracture, and electron-microscope fractography can be used effectively to examine these fractures.

Temper Brittleness

Temper brittleness is in many respects similar to 500 F embrittlement; however, it occurs at a somewhat higher temperature. Temper brittleness is usually detected in an impact test and occurs after heating in or slowly cooling through the approximate temperature range of 800 to 1050 F. Some of the characteristics of temper brittleness, which any theory must be capable of explaining, are as follows:

(1) Temper brittleness is not limited to martensitic microstructures; it also occurs in pearlite, bainite, or tempered martensite previously tempered at higher temperatures.

(2) Temper brittleness is manifested by a relatively high transition temperature, and is usually accompanied by a relatively low room-temperature impact strength.

(3) Toughness can be restored by reheating the steel above the embrittlement range and then cooling rapidly.

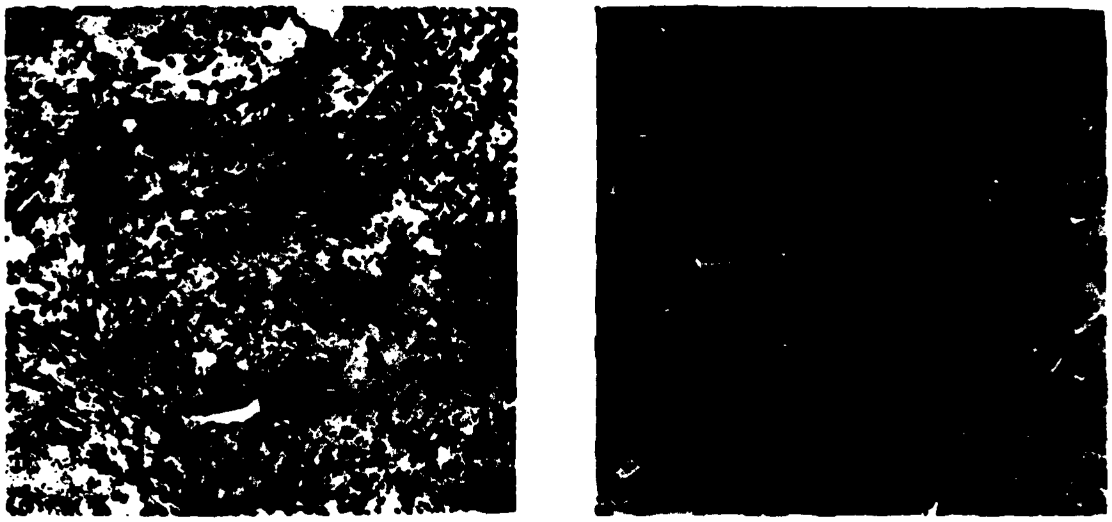
(4) Temper brittleness is time dependent, becoming more severe with prolonged tempering, and is most severe at about 950 F although it may be encountered throughout the range from 800 to 1050 F.

(5) Embrittlement can be retarded by using steels containing about 0.25 per cent molybdenum, or by using a somewhat more temper-resistant steel, together with a higher tempering temperature and rapid cooling after tempering.

(6) Temper brittleness is also dependent on the presence of minor elements in trace amounts.[7] A Ni-Cr steel and a Ni-Cr-Mo steel, essentially free of trace elements, were not susceptible to embrittlement within 1000 hours at 840 F. The presence of trace amounts of P, Sb, Sn, and As and larger amounts of Mn and Si promoted susceptibility, while trace amounts of Bi, Co, Cu, Ge, Ga, Zr, and N did not.

(7) The fracture of temper-brittle steels is essentially intergranular. Certain etching reagents will selectively etch the prior austenite grain boundaries of an embrittled steel.

Temper brittleness has been studied using electron-microscopic fractography. It is generally agreed that the fracture of steels in the temper-brittle state is intergranular, and that precipitate particles can be seen on the fracture surfaces. Hill and Martin[8] analyzed these particles in Ni-Cr steel containing antimony which was extremely susceptible to temper brittleness. Electron-microscopic fractographs of this steel in the temper-brittle condition are shown in Figure 4. X-ray-diffraction and fluorescence techniques revealed that the particles visible on the grain surfaces in Figure 4 were cementite with no detectable antimony content. Hill and Martin concluded that temper brittleness was closely associated with these lath-like particles but since they were free of antimony the particles could not be the initial cause of the brittleness. They suggest that the segregation of antimony to the grain boundaries promoted growth of the particles in the grain boundary, which could lead to an enrichment of segregate around each particle, reducing their interfacial energy and also the surface energy of the fracture faces.



1,500X 22,500X

FIGURE 4. ELECTRON-MICROSCOPIC FRACTOGRAPH OF AN ANTIMONY-CONTAINING Ni-Cr STEEL IN THE TEMPER-BRITTLE CONDITION SHOWING CEMENTITE PARTICLES ON THE GRAIN FACETS[8]

The steel was austenitized at 1650 F, oil quenched, tempered at 1150 F for 2 hours, water quenched, embrittled at 975 F for 4 hours, water quenched, and fractured in an IZOD impact test.

Another viewpoint is presented by Low[9] and by Orlov and Utevsky[10]. These authors claim that the fracture at low temperature of a steel in the tough or non-embrittled condition will be partially intergranular and partially transgranular (cleavage), and that these intergranular facets are identical with those in the same steel in the embrittled condition. Carbide particles of about the same size and morphology were found in both tough and brittle steels. Stated briefly, the responsibility for

temper brittleness cannot be attributed to the relatively large carbide particles that settle in the grain boundaries of tempered steels and subsequently appear on the intergranular fracture faces. This is contrary to the viewpoint expressed by Hill and Martin.

It is therefore suggested that temper brittleness may be a case of inherent grain-boundary weakness, possibly associated with segregation of impurities. Some evidence in support of this hypothesis was given by Plateau[11], who observed grain-facet striations after a 48-hour embrittling treatment (Figure 5). He felt such striations were evidence of adsorbed layers of impurity atoms on the grain boundaries.

FIGURE 5. INTERGRANULAR-FRACTURE SURFACE OF A STEEL, QUENCHED FROM 1562 F, TEMPERED AT 1202 F FOR 30 MINUTES, EMBRITTLED AT 932 F FOR 48 HOURS, SHOWING STRIATIONS INDICATIVE OF GRAIN-BOUNDARY ADSORPTION

SUMMARY

Both 500 F embrittlement and temper brittleness result in intergranular fracture along prior austenite grain boundaries. Since both of these embrittling reactions are grain-boundary phenomena, they must result from changes in the properties of the grain boundaries rather than from changes in the properties of the matrices. Both forms of embrittlement result in time-dependent elevation of the transition temperature, and both are promoted by the presence of certain minor elements in trace quantities. The use of electron-microscopic fractography in the study of these conditions has indicated that neither 500 F embrittlement nor temper brittleness can be attributed to precipitation of unique phases in the grain boundaries; no such phases have been observed or identified. There is some evidence, at least in the case of temper brittleness, that adsorbed layers of impurity atoms may be present on the grain boundaries. It is evident that further research employing electron-microscopic fractography, as well as other metallurgical tools, is needed before a complete understanding of these forms of embrittlement encountered in heat-treated steels can be achieved.

REFERENCES

(1) Klinger, L. J., Barnett, W. J., Frohmberg, R. P., and Troiano, A. R., "The Embrittlement of Alloy Steel at High-Strength Level", Transactions ASM, 46, p 1557 (1954).

(2) Nakashima, A. and Libsch, J. F., "Effect of Induction on 500° Embrittlement", Transactions ASM, 53, p 753 (1961).

(3) Capus, J. M., "The Influence of Trace Elements Upon the Impact Resistance of Low-Alloy Steels, Hardened and Tempered", Revue de Metallurgie, p 184 (August to September, 1959).

(4) Spretnak, J. W. and Bucher, J. H., preliminary information on an Air Force Contract (Nov. 30, 1963).

(5) Edwards, A. J. and Beachem, C. D., "Characterizing Fractures by Electron Fractography, Part X, Fractography of Notch Tensile Specimens of 4300-Series Steels", NRL Memorandum Report 1394 (February 1963).

(6) Backofen, W. A. and Ebner, M. L., "Metallurgical Aspects of Fracture at High Strength Level" WALTR 310.24/5-4, Final Report on DA-19-020-ORD-5235, (May, 1963).

(7) Steven, W. and Balajiva, K., "The Influence of Minor Elements on the Isothermal Embrittlement of Steels", Journal of the Iron and Steel Institute, 193, p 141 (October, 1959).

(8) Hill, R.G.C. and Martin, J. W., "A Fractographic Study of Some Temper-Brittle Steels", Metal Treatment and Drop Forging, 29, pp 301-306, 310 (August, 1962).

(9) Low, J. R. Jr., "A Review of the Microstructural Aspects of Cleavage Fracture" Fracture (Swampscott Conference, 1959), John Wiley and Sons, Inc., New York (1959).

(10) Orlov, L. G. and Utevskiy, L. M., "Electron-Microscope Examination of the Surface of Fractures Related to the Phenomenon of Temper Brittleness of Steel", Problems of Metallography and Physics of Metals, 5th Symposium, p 277 (1958).

(11) Plateau, J., Henry, G., and Crussard, C., "Influence of Physico-Chemical Conditions of Grain Boundaries on Intergranular Brittleness at Low Temperatures", Precipitation Processes in Steel (ISI Special Report No. 64), The Iron and Steel Institute (1959).

LIST OF DMIC MEMORANDA ISSUED
(Continued)

A list of DMIC Memoranda 1-164 may be obtained from DMIC, or see previously issued memoranda.

DMIC Memorandum Number	Title
165	Review of Uses for Depleted Uranium and Nonenergy Uses for Natural Uranium, February 1, 1963
166	Literature Survey on the Effect of Sonic and Ultrasonic Vibrations in Controlling Grain Size During Solidification of Steel Ingots and Weldments, May 15, 1963
167	Notes on Large-Size Furnaces for Heat Treating Metal Assemblies, May 24, 1963 (A Revision of DMIC Memo 63)
168	Some Observations on the Arc Melting of Tungsten, May 31, 1963
169	Weldability Studies of Three Commercial Columbium-Base Alloys, June 17, 1963
170	Creep of Columbium Alloys, June 24, 1963
171	A Tabulation of Designations, Properties, and Treatments of Titanium and Titanium Alloys, July 15, 1963
172	Production Problems Associated with Coating Refractory Metal Hardware for Aerospace Vehicles, July 26, 1963
173	Reactivity of Titanium with Gaseous N_2O_4 Under Conditions of Tensile Rupture, August 1, 1963
174	Some Design Aspects of Fracture in Flat Sheet Specimens and Cylindrical Pressure Vessels, August 9, 1963
175	Consideration of Steels with Over 150,000 psi Yield Strength for Deep-Submergence Hulls, August 16, 1963
176	Preparation and Properties of Fiber-Reinforced Structural Materials, August 22, 1963
177	Designations of Alloys for Aircraft and Missiles, September 4, 1963
178	Some Observations on the Distribution of Stress in the Vicinity of a Crack in the Center of a Plate, September 18, 1963
179	Short-Time Tensile Properties of the Co-20Cr-15W-10Ni Cobalt-Base Alloy, September 27, 1963
180	The Problem of Hydrogen in Steel, October 1, 1963
181	Report on the Third Maraging Steel Project Review, October 7, 1963
182	The Current Status of the Welding of Maraging Steels, October 16, 1963
183	The Current Status and 1970 Potential for Selected Defense Metals, October 31, 1963
184	A Review and Comparison of Alloys for Future Solid-Propellant Rocket-Motor Cases, November 15, 1963
185	Classification of DMIC Reports and Memoranda by Major Subject, January 15, 1964
186	A Review of Some Electron-Microscopic Fractographic Studies of Aluminum Alloys, February 5, 1964